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(54) Title: PARTICULATE POLYMERIC COMPOSITIONS AND THEIR PRODUCTION

(57) Abstract

Encapsulated particles comprise a core surrounded by a coacervate coating that comprises a low critical solution temperature polymer and a water removal depressant for the temperature of reversible insolubilisation of that polymer. The composition is either in the form of dry particles or is an aqueous dispersion at a temperature below the temperature of reversible insolubilisation of the polymer in the absence of the depressant but above the temperature of insolubilisation in the presence of the depressant. The coating dissolves when the composition is mixed with water. The composition is made by forming a dispersion of the core particles in a solution of the polymer, heating the solution to cause it to precipitate as a coacervate, and then adding the depressant. The composition can be an aqueous dispersion or dry particles.

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Particulate Polymeric Compositions and their Production

This invention relates to processes of encapsulating particles by coacervation and to products made by coacervation processes.

Coacervation techniques for encapsulating a variety of materials are well known and are described in, for instance, GB 1,275,712, 1,475,229 and 1,507,739 and DE 3,545,803. In such techniques, the particulate material is provided as a dispersion in a solution of coacervating polymer or polymer blend and the polymer or polymer blend is then caused to precipitate out from solution so as to form a coacervate coating around the individual particles. If the coacervation technique merely involves precipitation, the coating will tend to be reasonably permeable to water, and may even be readily soluble in water.

A particular problem arises when it is desired to have a coating which is wholly impermeable to water and to the coacervated material under some conditions, but to be readily permeable to water or to the coacervating material under other conditions. It is common to react permeable or soluble coatings chemically, for instance by cross linking during or after coacervation, so as to render it impermeable or to strengthen it. However, it is then generally too impermeable to release the coacervated material or to provide water permeability under the conditions that can conveniently be provided.

In particular, a coacervation technique is described in EP 356,239 for encapsulating within a polymeric shell particles consisting of a polymeric matrix containing a detergent protease and the resultant encapsulated particles are dispersed in a liquid detergent concentrate. Although this process is useful, it is difficult to obtain a polymeric shell that is sufficiently impermeable to enzyme and water to ensure stability of the enzyme within the

liquid detergent, but sufficiently soluble in warm water to release the enzyme when the detergent concentrate is diluted in wash water.

In EP 351,162 it is proposed to precipitate a water soluble polymer generally in the presence of an aqueous solution of enzyme. It is possible that some of the techniques described in EP 351,162 may give some form of coacervation but again it is difficult to form a coacervate shell that both protects the enzyme adequately during storage of the liquid detergent and releases it adequately upon dilution of the liquid detergent in wash water. For instance polyvinyl alcohol has been proposed as a matrix or a coating for enzyme particles but it is difficult to achieve a suitable balance of insolubility during storage and release when required.

In U.S. 3,244,640 it is proposed to encapsulate particles dispersed in an aqueous solution of a copolymer of an acrylamide and an N-alkyl acrylamide by heating the dispersion to effect coacervation. This process is possible because these copolymers belong to the class now known as "low critical solution temperature" (LCST) polymers. A characteristic of such polymers is that they can be in aqueous solution at one temperature but can be insolubilised reversibly by heating to a higher temperature, which is the "temperature of reversible insolubilisation" (TRI).

The coacervate coating by this technique tends to be rather weak and so it is proposed in U.S. 3,244,640 to add a cross linking agent to harden the coacervate polymeric coating that is formed, and then to recover and dry the encapsulated particles. It is also stated in U.S. 3,244,640 that it can be desirable to include inorganic salts such as alkali metal sulphate in the aqueous solution of the LCST polymer before heating so as to reduce the temperature of coacervation, and that it is possible to induce coacervation solely by the addition of inorganic salts. However it is stated to be preferable not to add

the salts because the capsules then have to be washed after recovery to remove residual salt. Also, when coacervation is brought about by adding a material to the coacervating solution, there is a tendency for agglomeration of polymer to occur in preference to uniform coacervation.

Coacervation techniques have been used for encapsulating a wide variety of particulate materials, often including solutions or dispersions of an active ingredient in a solid or liquid matrix. However, as indicated, known techniques have not proved entirely satisfactory for the situation where the coating must provide an impermeable barrier in one liquid environment and a permeable barrier in another liquid environment. Also, present techniques have tended to be inadequate for the encapsulation of some compositions. For instance some herbicides or other agriculturally useful, water insoluble, active ingredients that at present normally have to be delivered to the user as emulsifiable concentrates (that is to say emulsions in oil that have to be dispersed into water to make a sprayable composition) are difficult to encapsulate satisfactorily to give release when required.

There is therefore a need for a novel method of coacervating particles, and for novel products, that overcome these various disadvantages.

A process according to the invention for forming encapsulated particles comprising a core surrounded by a coacervate coating comprises

providing an aqueous solution of a LCST polymer that has a temperature of reversible insolubilisation (TRI) in that solution of T1,

forming a dispersion of the particles in that solution at a temperature T2 that is below T1,

heating the dispersion to a temperature above T1 and thereby precipitating the LCST polymer as a coacervate around the particles, then

adding a TRI depressant to the solution and thereby reducing the temperature of reversible insolubilisation of

the LCST polymer in that solution to a temperature T3 that is lower than T1, and

either cooling the dispersion to a temperature between T3 and T1 and maintaining the dispersion at a temperature between T3 and T1,

or separating the particles from the dispersion while at a temperature above T3.

The invention also provides a particulate composition comprising encapsulated particles each comprising a core surrounded by a coacervate coating that comprises an LCST polymer and a water-removable TRI depressant, wherein the composition either is in the form of dry particles or is an aqueous dispersion at a temperature that is below the temperature of reversible insolubilisation of the polymer in the absence of the TRI depressant but above the temperature of reversible insolubilisation of the polymer in the presence of the TRI depressant, whereby the coating dissolves when the composition is mixed with water. The particulate composition may be a dispersion in an aqueous solution of the TRI depressant (for instance a liquid detergent) or may be a dry powder that can be added to water.

The invention also includes methods of protecting an active ingredient by providing it within such particles and then mixing the particulate composition into sufficient water to dilute the concentration of TRI depressant sufficient to raise the temperature of reversible insolubilisation to a value at which the polymer coating will dissolve and release the active ingredient into the dilution of water.

The TRI depressant and its amount, are selected to give the desired depression in the temperature of reversible insolubilisation. Preferably it is an electrolyte.

A wide variety of electrolytes can be used but since satisfactory results are obtained with simple inorganic salts it is generally preferred to use them as part or all

of the electrolyte. Suitable salts include sodium, potassium, ammonium, calcium, magnesium and aluminium salts, particularly of carbonate, sulphate, chloride and nitrate. Some or all of the electrolyte can be anionic surfactant, for instance of the type conventionally present in a liquid detergent concentrate.

Typical amounts of salt that should be added are 2 to 30% based on the aqueous composition, or such as to give a 15:1 to 1:15 weight ratio of polymer:salt. The amount is preferably sufficient for T3 to be at least 5°C below the anticipated lowest temperature of storage. As mentioned, some electrolyte can be present in the initial solution, typically in an amount of 0 to 5% based on the initial solution, provided this does not depress T1 too much.

Generally T1 is at least 5°C higher than the anticipated temperature of usage, for instance the temperature of the dilution water into which the particles are to be dissolved.

Although we prefer to use an electrolyte for depressing the reversible insolubilisation temperature, any other material that has the desired depressant effect can be used. Generally they can all be characterised as being water-miscible non-solvents (in the absence of significant amounts of water) for the relevant LCST polymer. Examples include organic liquids such as lower alcohols, glycols and non-ionic surfactants. Particular examples are ethanol, glycerol, ethylene glycol, mono propylene glycol and ethoxylated octyl or nonyl phenol surfactants.

The LCST polymer can be a naturally occurring polymer such as certain cellulose derivatives, such as the methyl, hydroxy propyl, and mixed methyl/hydroxy propyl cellulose ethers. However it is generally preferred for the LCST polymer to be a synthetic polymer formed by polymerisation of what can be termed an LCST monomer either as a homopolymer or as a copolymer with a hydrophilic monomer that is present in an amount insufficient to cause T1 to be unacceptably high. Suitable LCST monomers include N-

alkylacrylamide, N,N-dialkylacrylamide, diacetone acrylamide, N-acryloylpyrrolidine, vinyl acetate, certain (meth) acrylate esters (especially hydroxypropyl esters), styrene, and various other vinyl monomers, especially N-vinylimidazoline and the like.

When the LCST polymer is a copolymer, the comonomer is usually hydrophilic and can be non-ionic or ionic. Suitable non-ionic monomers include acrylamide, hydroxyethyl acrylate, vinyl pyrollidone, or hydrolysed vinyl acetate.

Anionic or cationic monomer can be used in place of or in addition to the non-ionic comonomer to form a copolymer or terpolymer with the LCST monomer respectively. Suitable anionic monomers include ethylenically unsaturated carboxylic or sulphonic acid monomers, for example (meth) acrylic acid and alkaline salts thereof, and 2-acrylamido methyl propane sulphonic acid. Suitable cationic monomers include dialkylaminoalkyl (meth)acrylates and acrylamides as acid addition or quaternary ammonium salts, for example dialkylaminoethyl (meth)acrylate acid addition salts. One beneficial effect resulting from the use of cationic or anionic comonomer or termonomer is that their presence can prevent the coagulation and subsequent phase separation of the encapsulated particles which may occur in particularly high salt environments such as may exist in certain detergents.

The method of the invention relies upon the reversible insolubilisation by temperature change of an LCST polymer to form a coacervate coating, followed by the addition of a TRI depressant to modify the properties of the coating in a beneficial manner. Since the initial insolubilisation is by temperature change, this can be conducted homogeneously througout the composition and so can yield very uniform coacervation.

An essential modification of the coating is that the TRI depressant reduces the temperature of reversible insolubilisation of the coating. This means that the

temperature of the solution can be cooled below the temperature at which the coacervate coating was first formed without the coating being solubilised. This permits handling, storage and recovery at ambient temperatures.

Another modification is that the addition of the TRI depressant can tend to change other physical properties of the coating of the LCST polymer. In particular, it is easily possible to select an LCST polymer that forms a much harder and less permeable coating in the presence of an added electrolyte (as the TRI depressant) than in its absence. Thus the addition of the electrolyte will generally both reduce the temperature of reversible insolubilisation of the polymer and will render the coating much harder and less permeable than it would be in the absence of the electrolyte.

However, the effect is reversible since when the concentration of TRI depressant is sufficiently reduced, the temperature of reversible insolubilisation will then rise again to, or at least towards, the initial temperature T1 of reversible insolubilisation. Also, if the TRI depressant hardened the coating, the coating may tend to revert to its original softer and more permeable texture.

This reversibility, and the maintenance of a non-cross linked polymer structure, is advantageous as it promotes subsequent release of the core upon dilution in water, but if desired the coating can be cross linked after its formation. Suitable methods for cross linking coacervate polymer coatings are known.

The process can be conducted to form dry particles that are separated from the medium in which they were formed. Separation can be by, for instance filtration or centrifuging or decanting, often followed by fluid bed or other drying.

One benefit of the process is that the presence of the TRI depressant means that the particles can be separated at conveniently low temperatures and will have a sufficiently

hard texture during separation and drying to facilitate handling. Sufficient TRI depressant will be trapped in the coacervate coating to maintain this structure even after separation of the particles from the aqueous solution of TRI depressant (usually an electrolyte) in which they are formed. However when the dry particles are subsequently dispersed into water, the water will dissolve the TRI depressant from the coating so as to reduce the concentration of TRI depressant in the vicinity of the coacervate polymer.

This dissolution must occur to a sufficient extent to allow the coating to be softened and rendered permeable to the core or active ingredient in the core and often full dissolution occurs at the prevailing temperature. For instance this is valuable when the particles contain an active ingredient that is to be distributed into water, since the dry particles can be stirred into sufficient water to dilute the TRI depressant content sufficiently for the shell to dissolve and to release the active ingredient into water. This is particularly valuable for agricultural active ingredients such as herbicides or pesticides that, prior to the invention, might have had to be formulated as emulsifiable concentrates because they are insoluble or poorly soluble in water.

A particularly valuable aspect of the invention arises when the particles are to be maintained in the dispersion at a temperature between T1 and T3. As a result, provided the amount of electrolyte is such that T3 is below the normal ambient temperature, and therefore below the storage temperature of the dispersion, the coacervate coating will tend to provide a hard impermeable barrier during normal storage.

An example of this arises when the TRI depressant comprises electrolyte or other component in a liquid detergent concentrate. Thus the presence of this electrolyte or other component (and possibly additional electrolyte or other TRI depressant added for the initial

purpose of reducing the temperature of reversible insolubilisation) tends to maintain the coacervate coating in an impermeable form in the final dispersion containing the particles. However when the detergent concentrate is distributed into wash water, the concentration of electrolyte or other TRI depressant is diluted sufficiently to raise the temperature of reversible insolubilisation above the temperature of the wash water, with the result that the coacervate coating dissolves sufficiently to allow the release of the encapsulated material or active ingredient into the wash water. This is particularly valuable when the encapsulated particles contain a detergent enzyme.

The temperature T1 of reversible insolubilisation of the LCST polymer is the temperature at which the polymer will become insoluble if the solution containing the polymer is heated past T1 or will become soluble if insoluble polymer in that aqueous solution is cooled below that temperature. The temperature of reversible insolubilisation is generally reasonably abrupt, but may extend over a few degrees or more. Naturally T3 must be sufficiently low that any range for T1 does not significantly overlap the range for T3, which is the corresponding temperature for the polymer in the aqueous solution containing the TRI depressant. It should be noted that T1 and T3 relate to the polymer in the particular aqueous solution in which it exists. Thus, in the invention, the initial aqueous solution can contain some electrolyte or other TRI depressant in which event T1 in that solution will generally be lower than it would be if the initial solution had been free of electrolyte or other depressant, but additional electrolyte or other depressant is then added to reduce the temperature of reversible insolubilisation to T3.

T1 is generally at least 25°C and often at least 30°C and frequently is in the range 45 to 80°C but can be as high as 100°C. Some polymers require the presence of some

electrolyte in order to bring T1 in the initial solution down to a convenient value, eg below 100°C.

T3 is generally at least 5°C lower than T1 and is preferably at least 10°C and often at least 20°C below T1. When the particles are to be stored in aqueous electrolyte, T3 should be below the probable storage temperature. Preferably T3 is 0°C, that is to say the coating will never dissolve in liquid water, but higher values of T3, such as 5°C or even 10°C, can be acceptable in many instances.

The particles that are to serve as the core to be encapsulated can consist of a single component or a blend of components, typically a blend of an active ingredient in a carrier. The particles must be water-insoluble and capable of being dispersed in the aqueous solution of coacervating polymer. Accordingly the particles can be formed by dispersion of a water-insoluble oily solution or melt or by dispersion of water-insoluble finely divided solid.

When the core particles comprise or consist of an oily liquid or solution, they may include, for instance, paraffinic, napthenic or aromatic hydrocarbons, triglyceride oils or fats, silicone oils or phthalic esters. If such materials have a melting point above ambient, they may be included as a melt. Often an active ingredient is present in the core within a polymer, for instance being dispersed throughout a matrix polymer. If the polymer is relatively water impermeable, it may protect a water soluble or water sensitive active ingredient from dissolution into the aqueous coacervating solution. For instance an enzyme may be distributed within particles of a matrix polymer, for instance as described in EP 356,239.

Active ingredients that may be included, either alone or in solvents, melts or polymer solid particles, include leuco dyes (that may be present as solutions for pressure-sensitive paper), agricultural chemicals, perfumes, flavours, condiments, essential oils, bath oils, enzymes and bleaching agents.

The invention is of particular value with agricultural chemicals, and especially water insoluble agricultural chemicals. Such chemicals may be growth promoters, nutrients or pesticides, including herbicides, insecticides (including pheromones), fungicides, nematocides, etc. Prior to the invention, a normal way of supplying such compositions was as an emulsifiable concentrate, i.e., a solution of the active ingredient in an organic solvent that could be emulsified into water to form a sprayable composition. The organic solvents are undesirable. By the invention, it is now possible to supply such compositions as either dry particles or as aqueous dispersions, both of which are stable under ambient conditions but, when diluted with the water of a spray solution, release the active ingredient into the spray solution. Naturally suitable emulsifying agent may be required to maintain it in emulsion in the spray solution.

When the active ingredient is in a matrix polymer it can be preferred for the polymer to be in a water insoluble form within the particles so as to reduce still further the risk of solubilisation of the active ingredient through the coacervate coating, but preferably the matrix polymer should dissolve at the pH of the dilution water, so as to release the active ingredient. When the core particles comprise active ingredient dispersed in a matrix polymer, these particles will preferably have initially been formed as a dispersion of polymer particles in hydrophobic oil (as in EP 356,239) and this dispersion is then dispersed into the aqueous coacervating solution. Preferably the matrix polymer is sufficiently hydrophobic that it will partition into the oil in preference to the aqueous solution of the coacervating material. As a result the core particles comprise one or more matrix polymer particles surrounded by the oil, and the oil is surrounded by the coacervate shell. This is described in our application filed to-day reference 60/3213/01, claiming priority from GB 9110408.3. The

matrix polymer can be as described in that or in EP 356239. It can be an LCST polymer and the matrix can include a TRI.

The invention is performed by dispersing the desired particles into the aqueous solution of the coacervating, LCST, polymer at a temperature below T1 and under conditions that will provide a dispersion having the desired particle size. For instance when, as is often preferred, the dispersion is formed by dispersing an oil phase containing an active ingredient into the aqueous solution of LCST polymer, the act of dispersing the oil phase into the aqueous solution is generally conducted with sufficient agitation to form particles of the desired size. Usually the dispersion is formed in the absence of an emulsifying agent. By use of a homogenising system such as a Silverson mixer, it is possible to easily achieve a desired small particle size that is typically below 20μm and usually below 10μm, for instance down to 1μm or even 0.1μm. Similarly, if it is desired to make larger particles, for instance 50μm to 1mm, often 100μm or more, this can be achieved by appropriate choice of the homogenisation conditions.

If it is found that homogenisation does not lead to a stable emulsion of coacervated particles at a temperature at which a coacervate ought to have been achieved, this may be due to the amount of polymer being inadequate to form a proper coacervate coating around the core material, with the result that the coacervated system is unstable. Under these circumstances, the process should be repeated using a larger amount of coacervating polymer. The optimum amount will depend upon the particle size and the materials being used but is generally in the range 1:3 to 10:1 core material:capsule wall by dry weight.

To prevent the encapaulated particles of the invention coagulating and subsequently phase separating in the environment in which they are to be used, an entropic stabilising polymer, such as carboxymethyl cellulose, sodium alginates or starch, can be mixed with the LCST

polymeric component prior to encapsulation. Such polymers can act as dispersants in conditions of high salt concentration, eg in certain detergent environments.

The following are some examples.

Example 1 - Preparation of LCST copolymer

Diacetone acrylamide (1 part) and acrylamide (0.4 part) were dissolved in 1% aqueous sodium acetate at pH 6.5 (4.2 parts). This solution was purged with nitrogen for 45 min in a lagged reaction vessel fitted with a mechanical stirrer.

Polymerisation was initiated by addition of 5% aqueous ammonium persulphate (500 ppm) followed by 5% aqueous sodium metabisulphite (500 ppm). The course of the reaction was monitored by recording the temperature. After 30 min the temperature had risen from 20°C to a constant value of 70°C.

The mixture had become white and opaque and more viscous. On cooling a pale yellow clear viscous solution (25%) of Polymer A resulted.

By measuring the onset of turbidity of a 10% aqueous solution of Polymer A, the lower critical solution temperature (or temperature of reversible insolubilisation), was found to be 30°C.

Example 2 - Microencapsulation by simple coacervation of LCST polymer

An oil phase (33 parts) comprising a 5% solution of leuco-dye (Pergascript blue in Santosol oil from Ciba-Geigy and Monsanto UK respectively) was added with high shear mixing to 100 parts of an aqueous solution of Polymer A from Example 1.

The temperature was held below 20°C in all cases. After addition of the oil to the aqueous phase, the resultant smooth white O/W emulsion was warmed in a water-bath to 40°C and held at this temperature for 15 min. Aqueous sodium sulphate (10%; 5 parts) was added and the mixture then allowed to cool slowly to 20°C.

The process was repeated with variation of the concentration of Polymer A to give different capsules as listed below. Residual polymer in the aqueous phase was measured after centrifugation of each mixture, to show by difference how much had been deposited as capsule walls.

The amounts of polymer adsorbed in samples 2B, 2C and 2D were, respectively, 21, 35 and 51% by weight based on amount of polymer in the original solution and in each instance a stable emulsion was formed. In sample 2A, the amount of polymer added to the composition was less than the amount required to give the 21% absorption of sample 2B, the emulsion was unstable, and it was not possible to measure the polymer in the particles.

The average particle size in samples 2B to 2D was between 1 and 2μm with more than 95% by weight of the particles being below 5μm. Microscopic examination of the products of samples 2B to 2D under an optical microscope demonstrated the presence of distinct capsules having core regions and wall regions.

Example 3

The aqueous compositions of samples 2B to 2D are each added to liquid detergent concentrates comprising:

Alkyl benzene sulphonates 10%
Fatty alcohol ether sulphate 5%
Soap 1%
Alcohol ethylate 7%
Sodium citrate 7%
Sodium Xylene Sulphonate 8%
Water to 100%

They sre stored at approximately 20°C. Microscopic examination again shows the presence of the capsules that had been examined in the initial aqueous electrolyte in which they were formed, and suggests that there had been no change to the capsules.

When the resultant detergent is diluted with fifty times its volume of fresh water, no capsules are recovered when the mixture is subject to centrifugation and, instead,

it is apparent that the capsules have dissolved to release their contents.

Example 4 - Microencapsulation of Trifluralin

A polymer similar in composition to Polymer A was made by the procedure described in Example 1, but with a diacetone acrylamide:acrylamide weight ratio of 60:40. This polymer (Polymer B) had a TRI of about 50°C.

The 25% aqueous solution of Polymer B (1 part) was diluted with water (1.5 parts) and warmed to 45°C. A melt of technical Trifluralin (mp 40°C) (0.5 part) was added to the warm polymer solution and dispersed by high shear mixing into tiny drops of a dispersed phase. This mixture was then warmed to 65°C (a temperature above the polymer TRI) with low shear stirring. Sodium sulphate solution in water (10%; 0.25 part) was then added and the mixture allowed to cool slowly to 20°C).

The composition was stable on storage but, upon dilution with water, releases the trifluralin into the water to make a sprayable solution.

Example 5 - Microencapsulation by simple coacervation of LCST polymer using organic liquid to alter the temperature of insolubilisation

An oil phase (33 parts) comprising a 5% solution of leuco-dye (Pergascript blue in Santosol oil from Ciba-Geigy and Monsanto UK respectively) was added with high shear mixing to 100 parts of an aqueous solution of poly-N-isopropyl acrylamide.

The temperature was held below 20°C. After addition of oil to the aqueous phase, the resultant smooth white O/W emulsion was warmed in a water-bath to 40°C and held at this temperature for 15 min. Glycerol was added to 10% concentration based on the aqueous phase, and the mixture then allowed to cool slowly to 20°C.

A stable microcapsule suspension in water was obtained. The dye was released upon dilution with water.

CLAIMS

1. A process for forming encapsulated particles comprising a core surrounded by a coacervate coating, the process comprising

providing an aqueous solution of a low critical solution temperature (LCST) polymer that has a temperature of reversible insolubilisation (TRI) in that solution of T1,

forming a dispersion of the particles in that solution at a temperature T2 that is below T1,

heating the dispersion to a temperature above T1 and thereby precipitating the LCST polymer as a coacervate around the particles, then

adding a TRI depressant to the solution and thereby reducing the temperature of reversible insolubilisation of the LCST polymer in that solution to a temperature T3 that is lower than T1, and

either cooling the dispersion to a temperature between T3 and T1 and maintaining the dispersion at a temperature between T3 and T1,

or separating the particles from the dispersion while at a temperature above T3.

2. A process according to claim 1 in which the TRI depressant is selected from electrolytes and water miscible organic liquids that are non-solvents for the LCST polymer.

3. A process according to claim 1 in which the LCST polymer has T1 at least 30°C and T3 is not more than 10°C.

4. A process according to claim 1 in which the particles are separated from the dispersion while at a temperature above T3 and are dried.

5. A process according to claim 1 in which the particles are maintained in dispersion in the aqueous medium containing the TRI depressant.

6. A process according to claim 1 in which the core particles comprise an active ingredient selected from enzymes and agricultural active ingredients.

7. A process according to claim 1 in which the core particles comprise particles of a polymeric matrix in which active ingredient is dispersed.

8. A particulate composition comprising a core surrounded by a coacervate coating that comprises a low critical solution temperature (LCST) polymer having a temperature of reversible insolubilisation (TRI) and a water-removable TRI depressant, wherein the composition either is in the form of dry particles or is an aqueous dispersion at a temperature that is below the temperature of reversible insolubilisation of the LCST polymer in the absence of the TRI depressant but above the temperature of reversible insolubilsation of the polymer in the presence of the TRI depressant, whereby the coating dissolves when the composition is mixed with water.

9. A composition according to claim 8 in which the core comprises a water insoluble agricultural chemical, whereby upon dilution of the composition with water a sprayable emulsion of the chemical can be formed.

10. A composition according to claim 8 in which the active ingredient comprises a detergent enzyme.

11. A composition according to claim 10 which is a liquid detergent having a composition such that the LCST polymer remains impermeable to the enzyme during storage in the liquid detergent but releases the enzyme upon dilution of the liquid detergent with wash water.

12. A composition according to any of claims 8-11 in which the TRI depressant is selected from electrolytes and water miscible organic liquids that are non-solvents for the LCST polymer.

13. A composition according to any of claims 8-12 that has been made by forming the coacervate coating and then adding TRI depressant.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 92/00869

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.5 B 01 J 13/08

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl.5	B 01 J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	US,A,3567650 (J.A. BAKAN) 2 March 1971, see column 1, lines 50-70; column 2, lines 44-55; column 3, lines 15-20; column 4, lines 12-23; column 5, lines 35-43; column 6, lines 14-27; column 7, lines 60-75	1
X	US,A,3594326 (R.K. HIMMEL) 20 July 1971, see column 6, lines 33-57	1
A	EP,A,0246469 (HOECHST) 25 November 1987, see column 2, lines 35-55; column 13, lines 1-55; column 6, lines 16-33; column 7, lines 25-52	1,2,5,6,8,10,12
A	US,A,3244640 (P. STUDT et al.) 5 April 1966, see column 1, lines 48-66 (cited in the application)	1

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° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
14-07-1992	16. 09. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Natalie Weinberg

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 9200869 SA 59439

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 14/08/92
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82